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Preliminary communication

THE INTERACTION OF HEXAPHENYLCARBODIPHOSPHORANE WITH IRIDIUM OLEFIN CATIONS. METALATION OF COORDINATED LIGANDS[*]

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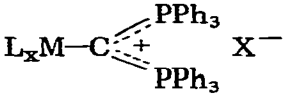
Hexaphenylcarbodiphosphorane [1, 2] (bis(triphenylphosphine)carbon, I) is a coordinatively unsaturated complex with a central carbon atom that can expand its coordination sphere by complexation to transition metals. The resultant complex II can potentially interact with coordinated ligands because of the high concentration of electron density on the carbon atom α to the transition metal atom.



(II)

The interaction of nucleophiles with non-conjugated dienes which are coordinated to transition metals can give diene displacements, addition to olefinic bonds, or coordination of the nucleophile to the metal atom with expulsion of anionic ligands. In contrast to the nickel triad, examples of nucleophilic attack on diene complexes of the cobalt triad are almost unknown [3]. We now report that I will induce self metalation[**] of Ir(COD)$^+$PF$_6^-$ (III)[***] (COD = 1,5-cyclooctadiene) and Ir(cyclooctene)$_2^+$ PF$_6^-$ under mild conditions to form π-allylic complexes. Thus a yellow-orange tetrahydrofuran (THF) solution of Ir(COD)$^+$PF$_6^-$ becomes bright red and gives a white precipitate when treated with a THF solution of I in a 1/1 molar ratio, respectively. The precipitate is identified as $[(C_6H_5)_3P]_2CH^+$ PF$_6^-$ (V) by IR ((PF$_6^-$) 840 cm^{-1}) and NMR (60 MHz; in $CDCl_3/CH_2Cl_2$, TMS as internal standard) (σ 1.70; t, *J*(PCH) 16 Hz 1H); 7.62 (m, *o*-C_6H_5, 12H), 7.52 (m, *m*,*p*-C_6H_5. 18H). Removal of excess THF

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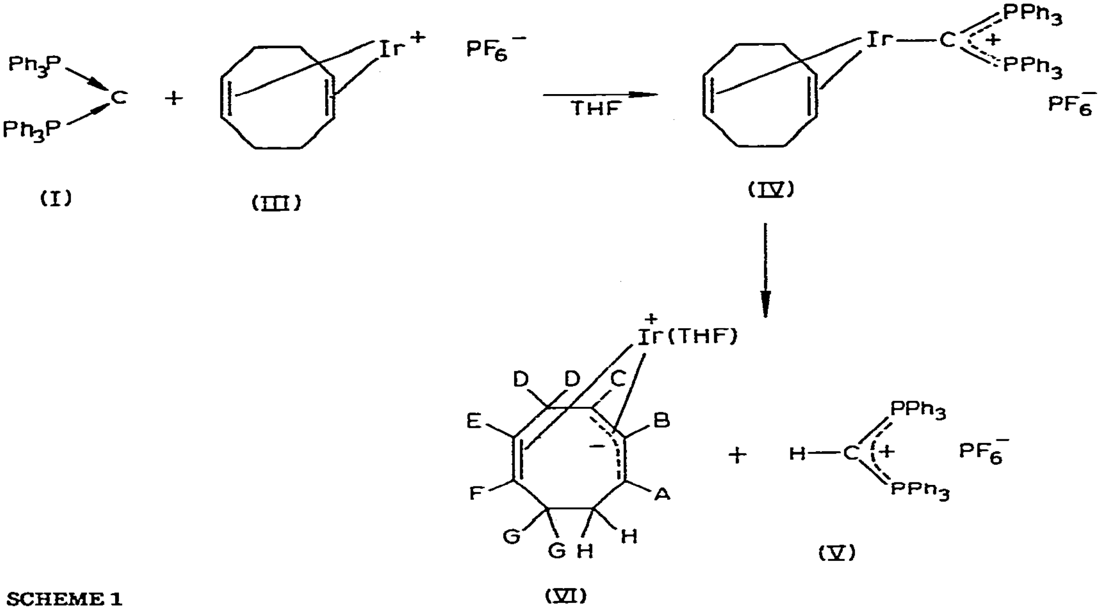
[**] Metalation is described as the transfer of a hydrogen atom from one carbon atom to another and replacement by a metal atom, albeit in this case π-allylic [4].

[***] The AgPF$_6$ must be absolutely dry; this was ascertained by the absence of γ(OH) 3500 cm^{-1} in the infrared spectrum [5].

after filtration gives a very air-sensitive red-orange solid VI (dec. 72-78°). The THF strongly coordinates to VI and cannot be completely removed by vacuum; an IR spectrum shows no presence of the PF_6^- ion (ν 840 cm^{-1}) or I. Scheme 1 is suggested to describe the metalation reaction.



SCHEME 1

The NMR spectrum of the red-orange solid in CH_2Cl_2 or DMSO-d_6 shows peaks which can be attributed to VI and THF (TMS internal standard), $\sigma(H_B)$ 4.80 (t, J 6 Hz, 1H); $\sigma(H_A)$ 3.92 (m, 1H); $\sigma(H_C)$ 3.66 (m, 1H); $\sigma(H_E)$ 2.28 (m, 1H); $\sigma(H_F)$ 2.02 (m, 1H); $\sigma(H_{D,H,G})$ 1.0-2.2 (m, 6H). These NMR spectra are consistent in many respects to (π-cyclopentadienyl)(η^3-cyclooctadienyl)iridium(I) complexes, especially if the chemical shift differences between cationic and anionic allylic complexes are taken into account [6]. In addition, these NMR spectra correspond to olefinic manganese carbonyl complexes recently studied by King and Ackermann [7].

The preparation of $Ir(COD)^+ PF_6^-$ in CH_2Cl_2 followed by treatment with I gives a blood-red solution whose NMR spectrum shows peaks which correspond to IV and VII. Vacuum removal of CH_2Cl_2 followed by addition of benzene-d_6 gives a white solid V and a red solution of VIII (Scheme 2). NMR (in C_6D_6, TMS as internal standard): $\sigma(H_A)$ 5.35 (t, J 6 Hz, 2H); $\sigma(H_B)$ 4.39 (t, J 6 Hz, 2H); $\sigma(H_C)$ 3.33 (t, J 6 Hz, 2H); $\sigma(H_{D,E})$ 1.9-2.16 (m, 6H)*.

A benzene solution of VI which was first prepared in THF and was stirred in benzene-d_6, showed NMR peaks attributable only to VI.

The preparation of $Ir(cyclooctene)_2{}^+PF_6^-$ (IX) was carried out in CH_2Cl_2 by the same method employed for $Ir(COD)^+PF_6^-$. Treatment of IX with I in CH_2Cl_2 resulted in a yellow-brown solution. Vacuum removal of CH_2Cl_2 followed by addition of C_6D_6 produced the white phosphonium salt V and a yellow solution of X (Scheme 3).

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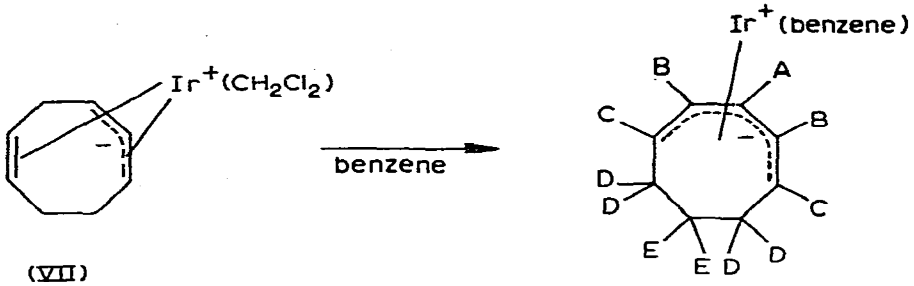
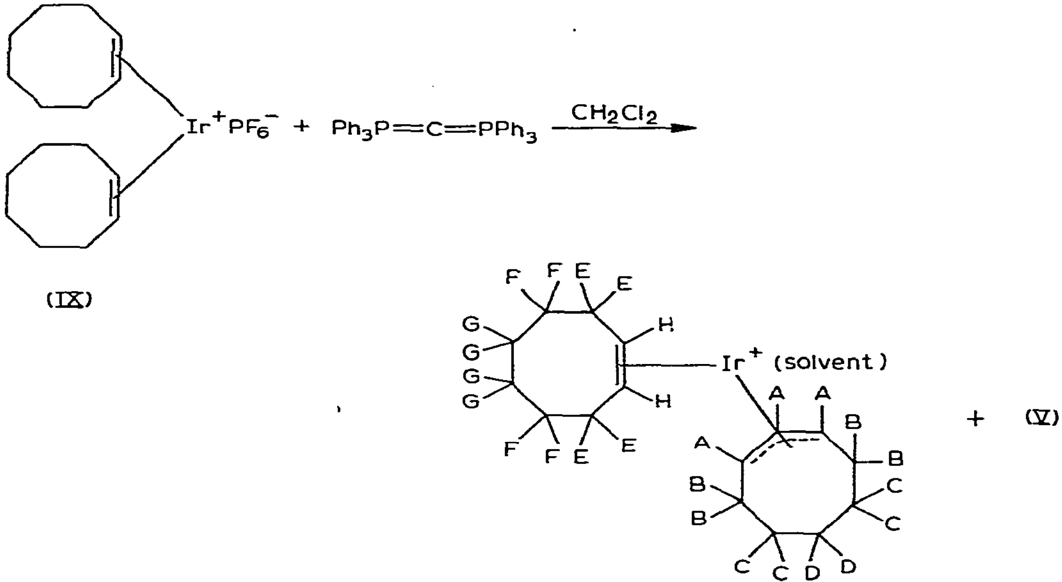
*Compound VIII could only be isolated as a benzene solvate. Elemental analyses reflect the presence of 1-2 molecules of associated benzene.



(VII)

SCHEME 2

(VIII)



(IX)

SCHEME 3

(X)

The NMR spectrum of X (in C_6D_6, TMS as internal standard) exhibited the following resonances: $\sigma(H_A)$ 3.60 (m, 3H); $\sigma(H_{B,E})$ 1.9-2.5 (m, 8H); $\sigma(H_{C,D,F,G})$ 1.08-1.83 (m, 14H); $\sigma(H_H)$ 6.25 (m, 2H). This agrees quite well with an allylic species such as X [7].

When $Ir(COD)^+PF_6^-$ is treated with benzene to form the arene cation, $Ir(COD)(\pi\text{-}C_6H_6)^+ PF_6^-$, followed by addition of I in a 1/1 molar ratio, no precipitate of V is obtained and no metalation observed. We propose that the treatment of III with I in THF or CH_2Cl_2 gives a transient complex such as IV (the corresponding complex would be obtained from IX and I) which induces metalation of the coordinated cyclooctadiene.

Although the process of hydrogen removal from the olefin ligand is not known, it is clear that the metal atom must remain coordinatively unsaturated for metalation to occur, since treatment of $Ir(COD)(\pi\text{-}C_6H_6)^+ PF_6^-$ with I does not produce V or VI. This could mean that a site on the metal atom is essential for the transfer of a proton from the olefin ligand to the coordinated carbodiphosphorane. Treatment of either 1,5-cyclooctadiene or cyclooctene with I does not result in abstraction of a proton from either olefin [8].

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